CHAPTER III
EXPERIMENTAL

3.1 Materials

In this study, natural rubber latex used as the substrate for admicellar polymerization was provided by Rubber Research Institute, ~ 60%DRC. Sodium dodecyl sulfate, 99% from Sigma®, was used as anionic surfactant for NR latex substrate. Pyrrole (Sigma®) was firstly purified by vacuum distillation and stored in refrigerator at about 4^0C before using in polymerization to achieve conductive polymer. 99.5% purity ammonium persulfate (Sigma®) was used as initiator without purification.

3.2 Equipment

NR latices were purified by centrifugation at 10000 rpm/ 20 min. with 2 cycles at 20^0C by centrifuge machine, Sorvall® model Super T21 from Dupont. Particle Size Analyzer (Mastersizer X®) was used to measure the particle size of NR latex particles (45 mm lens, an active beam length was set to 2.4 mm). Then, drop NR latex particles in a sample cell across a laser beam. Finally, the average particle size, particle size distribution, and specific surface area were obtained with the assumption of constant volume of spherical particle. Thermogravimetric analyzer (Dupont®, Model TGA 2950) was used to study the thermal stability and the decomposition temperature of the bare, coated latex particles, and NR latex/PPy composite. The morphology of the latex films and composites were observed by Optical Microscopy (Leica® model RMX) and Scanning Electron Microscopy (JOEL 5200®). The processability of the admicelled latex films was investigated by Melt Viscometer (Rheometrics® ARES). Tensile testing was carried out using Lloyd LRX® Universal Testing Machine under ASTM D882-91. Surface resistivity measurement proceeded following ASTM D257-92. The instruments used for

measuring surface resistivity were Resistivity Adapter (Keithley Model 6105), High Voltage Supply (Keithley 247), and Electrometer (Keithley 617).

3.3 Methodology

3.3.1 Particle Size Measurement

NR latex particles were analyzed for their particle size, size distribution, and the specific surface area after the purification of NR latex particles. (centrifuged for 20 min at 10000 rpm.)

3.3.2 Dry Rubber Content Measurement

Dry rubber content in percentage (%DRC) was measured following ASTM D1076-97. The purified NR latex was used to determine total solids content firstly before measuring dry rubber content. Air-oven was used to dry the samples at 70^0C for 18 h.

3.3.3 Polymerization of Pyrrole onto Latex Particles

3.3.3.1 One-step polymerization

NR latex particles were weighed at 3.9 g (controlled to the same weight of the previous work by Bunsomsit, K., *et al.*, 2002). The latex was then mixed with the prepared solutions (pH adjusted with HCl and NaOH to pH 3) to obtain the desired concentration of each substance in a whole solution of mixtures as shown in Table 3.1.

All mixtures were then agitated in a shaker bath at 30^0C for 6 h in order to allow SDS adsolubilization occurring on the surface of latex particles. Next, ammonium persulfate (equimolar amount based on pyrrole) was added into the mixtures to introduce polymerization of pyrrole inside the bilayer of SDS. Finally, after the 4 h polymerization of pyrrole, the mixtures (except N1) were dialyzed against a large volume of distilled water in order to remove traces of surfactants and salt. Then the admicelled latexes were cast at 40^0C in oven for 18 h followed by 70^0C for 18 h so as to obtain the smooth surface latex films having thickness of about 1 mm.

Table 3.1 Concentration of each substance in different mixtures

Sample	Pyrrole (mM)	SDS (mM)	NaCl (mM)
Ctrl. 1	-	8	0.31
Ctrl. 2	-	8	-
N1	5	-	-
N2-1	5	8	-
N2-2	10	8	-
N2-3	20	8	-
N2-4	40	8	-
N2-5	60	8	-
N3-1	5	8	0.31
N3-2	10	8	0.31
N3-3	20	8	0.31
N3-4	40	8	0.31
N3-5	60	8	0.31

3.3.3.2 Two-step polymerization

After finish admicellar polymerzation, the milky white emulsion was obtained, pyrrole of certain weight, e.g. 18 g was added to this emulsion with the certain amount of oxidant (equimolar amount based on pyrrole) and further polymerization. A series of N2-1, N2-2, N3-1, N3-2 was prepared first before doing a two-step polymerization. After that, the admicellar modified latex particles were weighed at 10, 20, 50, 60, and 80 wt% in order to mix with the pure freshly distilled pyrrole at the weight relative to that wt% of weighed admicelled latex. Then, the same method as one-step polymerization was carried out. Ammonium persulfate weighed to an equimolar amount of pyrrole was added into the mixtures after shaking in a shaker bath for 6 h at 30^0C. The mixtures were polymerized for 4 h and dried under the same procedures as the previous step.

3.3.4 Morphological Study

The samples obtained from two-step polymerization coated with gold were observed by SEM with magnification of 1500/ 20 kV. The other samples from admicellar polymerization and one-step process were prepared by dropping and spreading the milky or dark solutions after 4 h polymerization as thin as possible on glass slides and then drying in hood for 8 h. The thin films were investigated by using Optical Microscopy technique at ambient temperature with 200 and 500 magnifications. Pictures were taken by CCD camera using Qwin software.

3.3.5 Thermal Properties Measurement

All mixtures of the Admicellar modified latex, both one and two-step polymerization including PPy powder (prepared by chemical oxidation using ammonium persulfate as an oxidant), were tested for their thermal stability. The sample of about 8 mg was loaded in a platinum pan and held on a platinum wire under the furnace chamber using nitrogen atmosphere. The sample was heated from 30-600^{0}C with the heating rate of 10^{0}C/min. The nitrogen (oxygen was used once for PPy thermal stability in air) gas purge rate equaled 20 ml/min in furnace, and TGA nitrogen gas purge in the balance chamber equaled 30 ml/min.

3.3.6 FT-IR Obsevation of admicelled NR latex

FT-IR spectra of polypyrrole and some samples of the admicelled latex films were observed by FT-IR spectrometer (Bruker®, EQUINOX 55) so as to ensure the presence of PPy after the admicellar polymerization. The spectra obtained in the absorbance mode in a range of 400-4000 cm^{-1}. Spectra grade KBr, Carlo Erba®, was used as a background for PPy compressed film (using a hydraulic press under 8 kg/cm^2 for 2 minutes, with 1 cm in diameter and about 0.005 cm in palletized thickness). The background used for the admicelled latices, NR latex, and SDS was air.

3.3.7 Rheological Properties Measurement

All samples were cut into 25 mm disc with approximate thickness around 1 mm and tested by using the parallel plate geometry at a temperature of 70^{0}C. For the samples made from two-step polymerization, the resulting rubber sheet was

obtained by masticating for ~5 min by two-roll mill with no heat, then compressed at 70^0C, 2 min. After that, the sample was cooled for 1 min. Linear viscoelastic regime of every samples was firstly observed before measuring frequency sweep test at 70^0C with the frequency range from 0.1-100 s^{-1}.

3.3.8 Mechanical Properties Measurement

NR latex film, Ctrl. 1, Ctrl. 2, N2-1 to N2-4, and N3-1 to N3-3 were tested with the crosshead speed of 500 mm/min., and gauge length of 50 mm under room temperature using Lloyd Universal Testing machine. Unfortunately, samples from two-step at high PPy content were too hard and brittle to form into film so that mechanical test for the samples from two-step process were not carried out.

3.3.9 Conductivity Measurement

All samples were cut into round edge shape with 3 inches in diameter and tested for their surface resistivity following ASTM D257-92. The specimen was left at the temperature of 24^0C, 55% relative humidity. The dc voltage of 500 volt was applied to the specimen placed in the Resistivity Adapter Chamber for 1 minute. Then, the current was read and the surface resistivity was determined. Sample is in circular shape of 8.25 cm diameter.